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Metal measurement in aquatic environments by passive sampling methods: lessons learning from an *in situ* intercomparison exercise

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Abstract

Passive sampling devices (PS) are widely used for pollutant monitoring in water, but estimation of measurement uncertainties by PS has seldom been undertaken. The aim of this work was to identify key parameters governing PS measurements of metals and their dispersion. We report the results of an *in situ* intercomparison exercise on diffusive gradient in thin films (DGT) in surface waters. Interlaboratory uncertainties of time-weighted average (TWA) concentrations were satisfactory (from 28% to 112%) given the number of participating laboratories (10) and ultra-trace metal concentrations involved. Data dispersion of TWA concentrations was mainly explained by uncertainties generated during DGT handling and analytical procedure steps. We highlight that DGT handling is critical for metals such as Cd, Cr and Zn, implying that DGT assembly/dismantling should be performed in very clean conditions. Using a unique dataset, we demonstrated that DGT markedly lowered the LOQ in comparison to spot sampling and stressed the need for accurate data calculation.

Key words: DGT, uncertainty, blank, continental waters, coastal waters

42 **Capsule:** Metal concentrations obtained by DGT during an *in-situ* intercomparison exercise
43 showed that data dispersion was mainly explained by DGT handling and analytical procedure
44 steps.

45

46 **Highlights:**

47 Uncertainties on DGT results were assessed during an in-situ intercomparison exercise

48

49 DGT handling and analytical procedure steps are responsible for the dispersion of data

50

51 Data dispersion was similar between raw data and the TWA concentrations

52

53

54 **Introduction**

55

56 Reliable chemical monitoring of surface waters has become a crucial issue, especially
57 in the context of the Water Framework Directive (WFD). In particular, there is an emerging
58 need to find cheap and easy alternatives to spot sampling taking into account temporal
59 variability (e.g. flood events, seasons). Several tools have been developed over the years to
60 address this challenge, including bioassays/biosensors, biomonitors, chemical sensor probes
61 and passive samplers (PS).

62 The last 20 years have seen a surge in the development of PS to enable measurements
63 of a wide range of contaminants in surface waters (e.g. Vrana et al, 2014). PS tools carry
64 many advantages, as they (i) provide an integrated measure of the contamination over the
65 period of deployment, (ii) preconcentrate contaminants, which enables a lower limit of
66 quantification (LOQ) than classical analysis in spot samples and (iii) simplify the matrix of
67 the sample. Allan et al. (2006) showed that time-weighted average (TWA) concentrations
68 estimated by PS could be used to monitor long-term trends, to screen contaminants at very
69 low concentrations, and to identify sources of pollution. For metals, diffusive gradients in thin
70 films (DGT) and Chemcatcher[®] are the main PS devices used for monitoring surface waters
71 (Allan et al., 2008). The DGT device consists in a plastic piston loaded with a diffusive gel
72 layer backed by an ion-exchange resin gel (Chelex-100). The diffusive gel of the DGT allows
73 to measure metals in ionic form and weakly bound to small inorganic and organic complexes,
74 which represent a fraction of the total metal dissolved concentration (<0.45 μm), commonly
75 called the “labile” fraction. Metal accumulation in the resin is governed by the concentration
76 gradient established in the diffusive gel between the media and the resin. The TWA

77 concentration of the metal present in water over the period of exposure may be estimated as
78 follows:

$$79 \quad TWAC = \frac{m \cdot \Delta g}{D \cdot t \cdot A} \quad (1)$$

80 where m is the mass of metal accumulated in the receiving phase of the DGT (ng), Δg is the
81 thickness of the diffusive gel/filter (cm), D is the diffusion coefficient of the ionic metal in the
82 diffusive gel ($\text{cm}^2 \cdot \text{s}^{-1}$), t is the period of deployment (s), and A is the surface area (cm^2) of
83 DGT. For this calculation, only m has to be determined by the analytical step, as Δg , D , t and
84 A are generally known (DGT supplier and field data). The Chemcatcher[®] is constituted by a
85 standardized body combining a cellulose acetate membrane with a 47 mm Empore[™]
86 chelating disk for metals measurement. The uptake rates needed to calculate TWA
87 concentrations are less well known for Chemcatcher than the diffusive coefficient determined
88 for DGT (DGT Lancaster), and require element-specific uptake rate estimations in field
89 conditions (Neziri et al., 2011).

90 The DGT has a rapid response to fluctuating concentrations of Cd, Cu, Ni, Pb and Zn
91 during the period of deployment (Allan et al., 2007). For Cu, Zn and Pb, TWA concentrations
92 were in agreement with the filtered or ultrafiltered fractions obtained in spot samples and with
93 predicted inorganic and inorganic-fulvic acid associated metal fraction according to the visual
94 MINTEQ programme (Allan et al., 2007). Thus, DGT has been widely used as a speciation
95 tool for metals in freshwaters (Roig et al., 2011), coastal waters (Schintu et al., 2008), and
96 sediments (Dabrin et al., 2012). Several studies have focused on the applicability of DGT for
97 monitoring metals in freshwaters. Montero et al. (2012) reported that DGT gave reproducible
98 TWA concentrations for Cd, Cu, Ni and Zn in highly-fluctuating systems such as estuaries.
99 However, Buzier et al. (2014) reported that DGT monitoring of Cu, Cd, Ni and As in surface
100 waters requires stringent procedures to avoid DGT contamination and biases in the TWA
101 concentration estimation. Allan et al. (2008) also assessed Chemcatcher performances for
102 measuring Cd, Cu, Ni, Pb and Zn in surface waters. They reported that DGT and Chemcatcher
103 gave similar Cd and Zn concentrations to filtered samples, but both PS consistently
104 underestimated Cu and Ni concentrations and carried high measurement uncertainty for Pb
105 due to low sampler accumulation for this metal. Moreover, to improve validity of
106 Chemcatcher TWA concentrations, a performance reference compounds procedure was
107 needed to account for *in situ* turbulence, biofouling and temperature (Allan et al., 2008).

108 The upshot is that while both DGT and Chemcatcher are widely used for monitoring
109 metals in waters, there has been little effort to assess the uncertainty of their measurements.

110 To date, only one study has reported global results of an *in situ* intercomparison exercise on
111 several PS for priority pollutants (polycyclic aromatic hydrocarbons, pesticides and metals) in
112 surface waters (Miège et al. 2012). This first trial allowed to evaluate the representativeness
113 of PS for *in situ* monitoring and showed that despite the very low concentration levels, the
114 variety of tools and the different exposure and analytical strategies, global interlaboratory
115 dispersion was relatively low (relative standard deviation, RSD<100%). Nevertheless, this
116 work needed further investigations of results on metals measurements by DGT, particularly to
117 scrutinize sources of TWA concentration uncertainties, such as analytical and data treatment
118 steps.

119

120 **2. Strategy of the intercomparison exercise**

121

122 Ten laboratories with previous expertise in PS deployment participated in this
123 intercomparison exercise, i.e. ALS Scandinavia (SW), AZTI (SP), BRGM (FR), Cefas (UK),
124 Irstea Paris (FR), Irstea Lyon (FR), EDF R&D/LNHE (FR), IFREMER Toulon (FR), NIVA
125 (NO) and University of Cagliari (IT). Ten and 6 laboratories participated in the exercise for
126 metals at Ternay (France) and Thau (France), respectively. Each laboratory was asked to
127 provide its own samplers and apply its own methodology and strategy for PS
128 assembly/deployment, PS analytical treatment and TWA concentration calculation.

129 Field campaigns were led on two contrasted environments: one continental (Rhône
130 River, Ternay, France) and one coastal (Thau Lagoon, Hérault, France). All PS were deployed
131 7 days at Ternay (17–24 June 2010) and 9 days at Thau (27 April–5 May 2010). Details of the
132 exercise strategy are available in Miego et al. (2012).

133 Since some laboratories (3 at Ternay and 1 at Thau) exposed two types of PS for
134 metals, each laboratory code corresponds to the association of one laboratory and one tool.
135 The exposed PS were represented by DGT with open pores (OP) or restrictive pores (RP),
136 while only one Chemcatcher[®] was deployed at the Ternay site (Table 1). For each laboratory,
137 PS were exposed in triplicate together with one field blank (i.e. brought to the field but not
138 exposed in waters). Results from PS blanks (DGT/Chemcatcher laboratory blank) and from
139 the acid used for resin elution (acid blank) were also provided by each participant. Each
140 laboratory was asked to analyze 8 metals, i.e. Cd, Pb and Ni (priority substances of the WFD;
141 EC, 2013), Cr, Cu and Zn (substances on the French ecological status list; MEEDDM, 2010),
142 Mn and Co; and to provide information related to analytical performances (Table 2), diffusion
143 coefficients used (Table 3), resin elution, analytical procedure and calculation steps (Table 3).

144 In order to evaluate the accuracy and uncertainty of the analytical step, all participants
145 were provided with a reference solution (QC solution) that had to be analyzed in triplicate
146 (n=3) at the same time as PS eluate. The reference values for the QC solution were obtained
147 by isotope dilution coupled with inductively-coupled plasma mass spectrometry (ICP-MS).
148 Since Mn and Co have only one isotope, a standard addition method was used.

149 In order to compare TWA concentrations against total dissolved metal concentrations,
150 surface water samples were collected at the start, during and at the end of PS deployment.
151 Samples were collected in polypropylene bottles, immediately kept at 4°C, then filtered with
152 polyvinylidene difluoride (PVDF) filters (0.45 µm) previously cleaned in HNO₃ 10% (v/v).
153 At the Ternay site, filtrates were acidified with ultra-pure HNO₃ (0.5% v/v). At the Thau site,
154 due to the saline matrix, samples were preconcentrated by liquid-liquid extraction prior to
155 analysis (Danielsson et al., 1982). All samples were then analyzed by ICP-MS (Thermo X7,
156 Series^{II}).

157 A robust mean value and associated uncertainty was calculated for the QC solution
158 and the field-exposed PS according to ISO standard method 5725-5 (1994); Miège et al.,
159 (2012).

160

161 **3. Results and discussion**

162

163 3.1 The analytical step: the need for a clean room to avoid contaminations

164

165 In order to identify which step(s) could affect the dispersion of TWA concentrations
166 obtained by PS, a thorough evaluation of the analytical step was performed. Figure 1 displays
167 results of QC data from each laboratory with robust means and reference values of the QC
168 solution. The ratio between robust mean and reference value (expressed in percentage) varied
169 from 91% for Ni to 123% for Zn. Clearly, there was a lack of accuracy for Zn, since there was
170 no overlap between the reference value ± uncertainty of the QC solution (1.030 ± 0.036 µg/L)
171 and the robust mean (1.263 ± 0.130 µg/L). This is not surprising, since Zn is known to be one
172 of the most critical metals to analyze at low levels due to sample contamination at low level.
173 Since the QC solution had to be directly analyzed without pretreatment, this suggests that
174 sample and calibration solutions have to be handled in very clean conditions (clean room
175 and/or under a laminar flow hood) to minimize contamination. A recent intercomparison
176 exercise on surface water analysis at low-level concentrations (Zn=1 µg/L) involving 24
177 routine laboratories in France also showed a tendency to overestimate Zn concentrations

178 (139%) (Ghestem et al., 2012). Hence, these results confirm that laboratories liable to run PS
179 measurements must first learn to master contamination during the analytical step, especially
180 for Zn.

181
182 3.2 The choice of instrumental method for metal analyses: a crucial point to reduce
183 uncertainties

184
185 Zn, Cr, and Ni showed the highest analytical-step dispersion, at 24%, 22% and 16%,
186 respectively (Fig. 1). Our results are in accordance with the intercomparison exercise from
187 Ghestem et al. (2012) on water analysis, which also showed that at similar concentrations (Zn:
188 1 µg/L, Cr: 1.5 µg/L and Ni: 0.5 µg/L), RSDs were 23%, 13% and 17%, respectively. Here,
189 two laboratories (#E and #K) reported concentrations that were systematically far from the
190 reference values for Zn, Cr and Ni. In some cases, concentrations were also far from the
191 reference values for Cd, Co, Mn, Pb or Cu, for which one or both laboratories reported results
192 with poor accuracy or poor analytical repeatability. Table 2 details the analytical technique
193 and LOQ reported by each laboratory. Most laboratories used ICP-MS, whereas laboratories
194 #E and #K used graphite furnace atomic absorption spectrophotometry (GF/AAS). As
195 expected, LOQ was one order of magnitude lower for ICP-MS than for GF/AAS (Table 2),
196 which could explain the poor repeatability and/or accuracy for GF/AAS results at the µg/L
197 level. Therefore, laboratories need to analyze PS extracts with analytical instrumentation
198 combining high precision and sensitivity to ensure valid data for low-level metal
199 concentrations in environmental waters.

200
201 3.3 Blank control

202
203 Figure 2 reports the results for acid blanks, DGT laboratory blanks and Ternay-site
204 DGT field blanks as the mass of analyte in the eluates. For Mn, the mass in field blanks (mean
205 of 3.6 ng) was about 1% of the mass in Ternay-exposed DGT (mean: 306 ng) after the 7-day
206 deployment. For Co, Ni, Cu and Pb, the mean contribution of mass of metal in DGT field
207 blanks to the mass of metal in exposed DGT was 11%, 12%, 12% and 21%, respectively
208 (excluding laboratory #J for Co and Pb, which reported higher values). For Zn, Cd and Cr,
209 DGT field blank levels were high compared to the mass accumulated in DGTs exposed for 7
210 days in the river, representing mean contribution of 83%, 72% and 65%, respectively. In most
211 cases, the mass of metal in DGT field blanks could be explained by a contamination already

212 present in DGT laboratory blanks. Since the mass of metal was negligible in acid blanks (Fig.
213 2), this suggests that observed contaminations were mainly due to contamination of the resin
214 itself (during its preparation) and/or to the pre-elution resin handling step. These results
215 clearly show that the determination of TWA concentrations for trace metals such as Zn, Cd or
216 Cr is a delicate issue. For Zn, high blank levels in DGT were also reported by Munksgaard et
217 al. (2003). However, Sigg et al. (2006) also reported blank values in commercially available
218 DGT for Zn which were lower (32 ± 55 ng) than those obtained during this intercomparison
219 exercise (137 ± 242 ng). It is possible to subtract DGT laboratory blank from results obtained
220 for exposed DGT, but only if the results for DGT laboratory blanks are sufficiently
221 reproducible. To overcome this problem, a deployment over several weeks could enable to
222 trap a significantly higher mass of Zn, Cd and Cr than the mass initially present in DGT
223 laboratory blanks. Alternatively, Buzier et al. (2014) proposed to determine a LOQ-DGT
224 value representing the lowest mass of metal that could be quantified without a significant
225 blank contribution. This LOQ-DGT value was determined as the mean of DGT field blanks
226 ($n=44$) and 10-fold the standard deviation ($\text{mean} \pm 10 \times \text{SD}$). In our case study, this approach
227 could have been an interesting alternative but it would have required each laboratory to
228 determine its own LOQ-DGT by analyzing several DGT laboratory blanks.

229 Clearly, there is a need to improve the DGT measurement protocol in terms of blanks
230 and risk of contamination. Improvement hinges on clean conditions (e.g. cleanroom, laminar
231 flow hood), precise estimation of global contamination, and a methodology for factoring these
232 blanks into the final result. In our opinion, the estimation of LOQ-DGT appears to be the best
233 way forward on this issue.

234

235 3.4 Effect of LOQ decrease

236

237 One asset offered by PS is the possibility to decrease LOQ by preconcentrating the
238 metal on the receiving phase, which this intercomparison exercise has demonstrated as a
239 powerful advantage of PS devices. For Cd, for example, analytical LOQ averaged 32 ng.L^{-1} in
240 spot samples (Table 2); but, when DGT was applied with the average elution volume
241 (4.05 mL), average dilution factor (6.4), average diffusion coefficient of Cd at 20°C ($5.3 \cdot 10^{-6}$
242 $\text{cm}^2 \cdot \text{s}^{-1}$), average diffusive gel thickness (0.94 mm) and a period of deployment of 7 days
243 ($604\,800$ s), the LOQ for Cd was reduced to 0.80 ng/L . This means that DGT could decrease
244 LOQ by a factor ~ 40 . Another asset of PS is related to its application in coastal or marine
245 environments. Indeed, the PS devices investigated allowed to directly measure metals at ultra-

246 trace levels in coastal waters and, contrary to spot water samples direct analysis, which
247 requires an extraction step for eliminating the saline matrix that potentially induces analytical
248 interferences (i.e. Danielsson et al., 1982).

249

250 3.5 Exploration of usual practices

251

252 3.5.1 The PS extract dilution factor before analysis

253

254 Table 1 shows the volume of elution and the dilution factor applied by each laboratory
255 to prepare the PS extract. These parameters ranged from 1 to 10 mL (elution volume) and
256 from 1 to 10 (dilution factor). For example, if each laboratory was handed the same PS with
257 an amount of 1 ng of metal for analysis, the actual combination of volumes of elution and
258 dilutions factor used by laboratories would have given a metal concentration in the eluate
259 ranging from 0.020 to 1 $\mu\text{g/L}$, which underlines the huge variation in laboratory practices.
260 These different practices mainly reflect laboratory habits and are also justified according to
261 their analytical LOQ, and to the percentage of nitric acid concentration required in the final
262 eluent solution. Thus, applying a small volume of eluent and minimizing the dilution factor
263 before analysis could drastically concentrate metals before analysis. The choice of the these
264 two steps also highly depends on the compromise which was chosen by each laboratory: (i)
265 obtain a more diluted sample in a large volume, which leaves the possibility to perform
266 several replicates of analysis or (ii) obtain a more concentrated sample but in a small volume;
267 thus, leaving no second chance to perform replicate analysis. These are the two crucial steps
268 in DGT extract preparation for which good practice could radically reduce problems linked to
269 contamination and decrease analytical uncertainty. These different analytical protocol-related
270 practices can lead to very different (up to a factor of 50) measured final concentrations and to
271 variation in the defined LOQ for PS.

272

273 3.5.2 Correction of the PS extraction yield

274

275 In order to evaluate the mass of metal on the resin, most laboratories applied a
276 correction factor called “elution factor” to take into account partial extraction from the resin.
277 As presented in Table 1, most laboratories applied an elution factor of 0.8, as provided by the
278 DGT manufacturer. However, two laboratories (#C and #D) did not correct DGT data by an
279 elution factor, and one laboratory (#K) did not correct DGT data for Cd, yet applied an elution

280 factor of 0.7 for Pb. In fact, the two laboratories that used an elution factor of 1 were those
281 that also used the highest volume of elution (10 mL). Unfortunately, this elution factor of 0.8
282 provided by the DGT supplier was mainly applied by laboratories that used the most disparate
283 conditions. Given the broad differences in elution practice, this “common” empirical
284 extraction yield emerges as a key factor of dispersion in DGT measurement (RSD of 20%
285 with or without correction, as observed in this study); which suggests the need for either intra-
286 laboratory estimation of extraction yield or the development of an elution protocol leading to
287 “total extraction” of metals from the resin.

288

289 3.5.3 Influence of PS model constants: diffusion coefficient, gel thickness, DGT surface area

290

291 The diffusion coefficients (D) applied by each laboratory to calculate TWA
292 concentrations (Eq.1) from DGT results are reported in Table 3. Even though the trial
293 organizer provided the mean temperature of the exposure period at both sites (19.8°C at
294 Ternay site; 17.9°C at Thau site) to all laboratories, the diffusion coefficients used by each
295 laboratory were quite variable. For example, at Ternay site for Pb and for DGT-OP,
296 laboratory #B applied a diffusion coefficient of $6.29 \cdot 10^{-6}$ cm²/s whereas laboratory #D used a
297 value of $10.0 \cdot 10^{-6}$ cm²/s. In fact, for both the Ternay and Thau sites, the ratio between the
298 minimum and maximum value of diffusion coefficients applied for a same metal ranged from
299 1.3 for Cd to 1.6 for Pb. This large variation in diffusion coefficients is explained by the fact
300 that some laboratories (i.e. laboratory #E) had prepared their own diffusive gels and
301 characterized metal diffusion coefficients for their own gel. DGT-RP was deployed by two
302 laboratories who applied a diffusion coefficient that represents 70% of the diffusion
303 coefficients used for DGT-OP (Scally et al., 2003).

304 Concerning the other coefficients of the equation (Eq.1), gel thickness (Δg) values
305 applied by each laboratory were fairly similar, ranging from 0.76 mm to 0.94 mm and varying
306 according to the different DGTs used. Also, surface area of DGT (A) was similar (3.14 cm²)
307 for all DGTs purchased from DGT Research Limited, Lancaster (Table 1). However, some
308 laboratories applied different surface areas to calculate TWA concentrations for DGT-OP and
309 DGT-RP (#L and #G: 3.80 cm²; #D 4.91 cm²). The 3.80 cm² area represents the effective
310 sampling area provided by Warnken et al. (2006) when a diffusive boundary layer (DBL) is
311 taken into account; while the value of 4.91 cm² used by one laboratory (#D) is a wrong value,
312 since it represents the total surface area of the filter. In this case, the total diffusion layer
313 comprises the filter and the gel layer (Δg) plus the DBL thickness δ (0.2 mm in well-stirred

314 cases). Even if the surface area applied by laboratory #D was 56% higher than by the other
315 laboratories, the TWA concentrations calculated were not identified as outlier (Fig. 4 and 5),
316 suggesting that this term of the equation had no impact on the final result of this laboratory.

317 For example, we applied different combinations of data in the model calculation from
318 raw data obtained by laboratory #F for Cu at Ternay site. By applying a thickness of 0.91 mm
319 (gel + filter), a surface area of 3.14 cm² and by neglecting the DBL, this laboratory obtained a
320 TWA concentration of 0.305 µg/L. If the thickness of the filter was neglected, result should
321 have been 16% lower (0.254 µg/L). By applying a DBL of 0.2 mm and an adapted surface
322 area of 3.8 cm², TWA concentration should have been equal to 0.307 µg/L, which is close to
323 the initial result. In an another case, if a DBL was added (0.2 mm) to the model calculation
324 without changing the surface area, TWA concentration should have been equal to 0.372 µg/L
325 which is 22% higher than initial result. These simulations of various combinations of data
326 inputs lead to TWA concentrations ranging from 0.254 to 0.372 µg/L, which correspond to
327 the range of data obtained at Ternay site for laboratories (Figure 4) which did not exhibit
328 outliers' for TWA data.

329

330 3.6 Dispersion of PS measurements

331

332 3.6.1 Comparison between concentrations in ng/tool and TWA concentrations

333

334 Figure 3 gives the RSD (%) of Ternay-site and Thau-site data expressed in ng/tool and
335 for TWA (µg/L). Considering all the sampling and analytical steps, the dispersion of data in
336 ng/tool was very satisfactory for Mn, Ni and Cu, with a RSD lower than 18% and 35% at
337 Ternay and Thau, respectively. For Co, the dispersion of data in ng/tool at Thau site was also
338 very satisfactory (14%) but climbed to an unsatisfactory 64% at Ternay. For Mn, Cu and Co,
339 good reproducibility and accuracy was reported for the QC solution (Cf. 3.1, 3.2). Moreover,
340 we observed little contamination of DGT blanks (Figure 2) for these metals, thus resulting in
341 little dispersion of TWA data. In contrast, for Pb, the RSD in ng/tool was higher, reaching
342 31% and 48% at Ternay and Thau, respectively. Also, data dispersion was higher for Zn, Cd
343 and Cr, ranging from 40% to 88% at Ternay and from 69% to 111% at Thau. The high
344 dispersions in the mass of metals in ng/tool for Zn, Cd and Cr suggest that contamination
345 issues, as previously discussed, were the main sources of dispersion in TWA concentrations.

346 TWA concentration (Figure 3) followed similar data dispersion patterns as ng/tool. At
347 Ternay for example, RSD for Cu was 18% in ng/tool while RSD of TWA concentration was

348 15%. At Thau, the dispersion of Cd in ng/tool (111%) was close to that of TWA concentration
349 (101%). Also, data dispersion was reduced, by 21% for Co at Ternay site and by 27% for Cr
350 at Thau site, suggesting that dispersion in ng/tool could be reduced by data used as model
351 inputs. Since data dispersion was similar between data in ng/tool and in TWA concentration,
352 this suggests that whatever the data used as model inputs by laboratories, calculation was
353 proportional, dispersion of data being mainly driven by DGT handling and analytical steps.
354 Although laboratories used different values for certain parameters like diffusion coefficient,
355 gel thickness or surface area (Table 1 and 3), the calculation step did not lead to any greater
356 dispersion of the data. This suggests that the different coefficients needed to calculate TWA
357 concentration did not add significant dispersion over that calculated for DGT accumulated
358 mass. Thus, even if diffusive coefficient values could vary (Table 3) since they are specific to
359 the gel used by each participant, they allowed leading to a similar TWA concentration.

360

361 3.6.2 Dispersion of TWA concentrations compared to single analyses

362

363 The dispersion of the TWA concentrations obtained during this intercomparison
364 exercise was compared against that obtained in one international proficiency test on
365 freshwaters spiked with selected metals (Table 4; Brunori et al., 2007). The comparison
366 showed higher RSDs for Zn (79-99%), Pb (58-112%) and Mn (28-35) measured by DGT. For
367 Zn and Pb, these higher RSDs could be explained by biases induced by the PS itself, during
368 field deployment (e.g. contamination of PS) and by the low level of concentrations in these
369 two environments (spot sampling: from 0.67 to 1.80 $\mu\text{g/L}$ for Zn and from 0.02 to 0.37 $\mu\text{g/L}$
370 for Pb). For Mn, the RSD was lower for the proficiency testing (11%) than for this *in situ* PS
371 exercise (28%), probably since proficiency testing was led with 44-fold higher water
372 concentrations than our TWA concentrations. For Cu, Cr and Cd, PS gave similar dispersion
373 as the RSD of the proficiency testing dataset; whereas for Ni, PS gave lower dispersion (41%)
374 compared to proficiency testing (75%). To conclude, the data dispersion on TWA
375 concentration obtained during this PS intercomparison proved very satisfactory given the
376 different laboratories, different tools, *in situ* deployment and ultra-trace concentrations of
377 metals in these two environments (e.g. Cd $\sim 12 \text{ ng.L}^{-1}$).

378

379 3.6.3 Comparison of dispersion in TWA concentrations according to laboratory and type of

380 PS

381

382 Figures 4 and 5 plot TWA concentrations obtained by each laboratory and tool at the
383 Ternay and Thau sites, respectively. Robust means of TWA concentrations obtained for all
384 laboratories are also displayed. At Ternay, only one Chemcatcher was deployed during the
385 intercomparison exercise and results were only reported for Cd, Cu, Ni, Pb and Zn. Despite
386 satisfactory QC results, TWA concentrations obtained with Chemcatcher nevertheless
387 included some outliers (Cochran test), notably for Cd, Pb and Zn. Unfortunately, with only
388 one dataset, the lack of comparison rules out any definitive conclusions on interlaboratory
389 dispersion for Chemcatcher.

390 Theoretically, DGT-RP allows the diffusion of free ions and small organic complexes,
391 while DGT-OP also allows the diffusion of metals associated with large organic ligands. In
392 fact, Allan et al. (2007) demonstrated that combining DGT-RP with DGT-OP allows to assess
393 the metal fraction linked to large organic ligands. Nonetheless, results obtained for DGT-OP
394 and DGT-RP by the same laboratory (*#F and #M*) at Ternay were not significantly different
395 for any of the selected metals (Figure 4). It is difficult to reach a conclusion for the other
396 laboratories (*#G and #L*), since in most cases (Cr, Co, Cu, Mn, Ni and Pb) TWA
397 concentrations from DGT-RP and/or DGT-OP showed high dispersion according to Cochran
398 and/or Grubbs tests. For Cd and Zn, we found no significant differences between DGT-OP
399 and DGT-RP. These results suggest that, in this specific context, it was difficult to
400 discriminate labile metals (free ions and small inorganic complexes) from metals associated
401 with large organic ligands, even when the analyses were performed by the same laboratory.

402

403 4. Conclusion

404

405 This in-situ intercomparison exercise on PS for metal analysis in surface waters provided, to
406 our knowledge, a first attempt to identify key parameters controlling TWA metal
407 concentrations estimation and to quantify uncertainties and evaluate their main sources/origin.
408 We clearly demonstrated that DGT handling and analytical procedure steps are responsible
409 for the dispersion of data. Thus, it is necessary that laboratories using such passive samplers
410 for trace metal analysis master contamination by using a clean room (Class 100) for all
411 analytical steps, from the assembly of the DGT tool, their dismantling and elution, to the
412 analysis of eluates. Moreover, laboratories must analyze PS extracts with analytical
413 instrumentation combining high precision and sensitivity to ensure valid data, allowing
414 applying large combination of elution volume and dilution before analysis. For natural marine
415 and fresh waters, the use of ICP-MS is highly recommended. Finally, we showed that

416 whatever the data inputs (i.e., diffusive coefficient, elution factor from bibliography for
417 purchased DGT, or determined in laboratory for home made DGT) which were used by
418 laboratories in model calculation, data dispersion was similar between raw data obtained in
419 ng/tool and the TWA concentrations.

420

421 **Acknowledgements**

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424 of the central laboratories for water analysis: Metrological Reference Laboratory (LNE) for
425 QC solutions, Irstea at Lyon (metals, physical-chemical parameters at Ternay), IFREMER at
426 Sète (physical-chemical parameters at Thau), IFREMER at Nantes (metals at Thau).

427

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Table captions

609 Table 1: Type and characteristics of passive sampler and extraction steps before analysis used
610 by each laboratory at the two deployment sites.

611 (1) DGTOP: DGT with a diffusive gel with open pores (~ 5 nm), DGT-RP: DGT with a diffusive gel with
612 restrictive pores (~ 1 nm)

613 nd : not determined

614 Laboratories were identified (by *, # and □) when they deployed two types of tools.

615
616 Table 2: Analytical technique and limit of quantification (LOQ) of each laboratory.
617 Laboratories were identified (by *, # and □) when they deployed two types of tools.

618 LOQ were determined according to NF T90-210 (AFNOR, 2009) or were equal to $\text{Mean}_{\text{blank}} +$
619 $10 \cdot \text{SD}_{\text{blank}}$.

620
621 Table 3: Diffusion coefficient used by each laboratory to calculate time weighted average
622 concentration (TWA). Laboratories were identified (by *, # and □) when they deployed two
623 types of tools.

624
625 Table 4: Comparison of relative standard deviation (RSD) for metal concentrations between
626 this PS intercomparison exercise at Ternay/Thau sites and the SWIFT-WFD proficiency
627 testing exercise on natural waters (Brunori et al., 2007).

628 x*: robust mean, SD: standard deviation of the robust mean, RSD: relative standard deviation.

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631 **Figure captions**

632
633 Figure 1: Metal concentration (mean \pm SD, n = 3) measured by each laboratory, with
634 interlaboratory robust mean (dotted line) and reference concentration (solid line) for the
635 quality control (QC) solution.

636
637 Figure 2: Amount of metal in acid blank, DGT lab blank, DGT field blank and DGT exposed
638 in situ at Ternay site after 7 days of exposure for each laboratory.

639
640 Figure 3: Relative standard deviations (in %) of DGT data (without QC outliers) in ng/tool
641 (solid line) and for TWA concentration in $\mu\text{g/L}$ (grey area), for Cd, Cr, Co, Cu, Mn, Ni, Pb
642 and Zn at Ternay (A) and Thau (B) sites.

643
644 Figure 4: TWA concentration of each laboratory, robust mean (dotted lines) and spot
645 sampling mean concentration (solid line) for Cd, Cr, Co, Cu, Mn, Ni, Pb and Zn at Ternay
646 site. Laboratories were marked when outliers were identified by Cochran (within laboratory
647 variability) and Grubbs tests (between laboratory variability) for QC and TWA data; QC data:
648 ○ Cochran test, ● Grubbs test - TWA data: □ Cochran test, ■ Grubbs test.

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650 Figure 5: TWA concentration of each laboratory, robust mean (dotted lines) and spot
651 sampling mean concentration (solid line) for Cd, Cr, Co, Cu, Mn, Ni, Pb and Zn at Thau site.
652 Laboratories were marked when outliers were identified by Cochran (within laboratory
653 variability) and Grubbs test (between laboratory variability) for QC and TWA data; QC data:
654 ○ Cochran test, ● Grubbs test - TWA data: □ Cochran test, ■ Grubbs test.

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Lab code	PS tool	Ternay Site	Thau Site	Binding agent	Gel thickness (mm)	Surface area (cm ²)	Volume elution (ml)	Volume resin (ml)	Dilution before analysis	Elution factor	Analysis
A	DGT-OP	•	•	Chelex-100	0.94	3.14	1.0	0.15	10	0.8	ICP/MS
B	DGT-OP	•	•	Chelex-100	0.80	3.14	1.8	0.16	10	0.8	ICP/MS
C	DGT-OP	•	•	Chelex-100	0.80	3.14	10	0	5.0	1.0	ICP/MS
D	DGT-OP	•	•	Chelex-100	0.78	4.91	10	0.20	nd	1.0	ICP/MS
E	DGT-OP	•		Chelex-100	0.76	3.14	1.0	0.16	nd	0.8	GF/AAS
F*	DGT-OP	•	•	Chelex-100	0.78	3.14	2.5	0.15	3.5	0.8	ICP/MS
G [#]	DGT-OP	•		Chelex-100	0.78	3.80	1.0	0.16	3.0	0.8	ICP/MS
H [□]	Chemcatcher	•		Empore chelating disk	nd	nd	nd	nd	10	nd	ICP/MS
I [□]	DGT-OP	•		Chelex-100	0.90	3.14	1.0	0.16	10	0.8	ICP/MS
J	DGT-OP	•		Chelex-100	0.76	3.14	10	0.15	nd	0.8	ICP/MS
K	DGT-OP	•	•	Chelex-100	0.76	3.14	4.5	0.15	nd	0.8 (Cd: 1, Pb: 0.7)	GF/AAS
L [#]	DGT-RP	•		Chelex-100	0.78	3.80	1.0	0.16	3.0	0.8	ICP/MS
M*	DGT-RP	•	•	Chelex-100	0.78	3.14	2.5	0.15	3.5	0.8	ICP/MS

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Table 1

Lab code	Analysis	Analytical LOQ (µg/L)							
		Cd	Cr	Co	Cu	Mn	Ni	Pb	Zn
A	ICP/MS	0.058	0.160	-	0.066	0.210	0.086	0.044	0.80
B	ICP/MS	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010
C	ICP/MS	0.002	0.010	0.005	0.10	0.030	0.050	0.010	0.20
D	ICP/MS	0.020	0.300	0.020	0.03	0.200	0.200	0.020	0.20
E	GF/AAS	0.010	0.200	-	0.20	-	0.400	0.120	-
F*	ICP/MS	0.010	0.050	0.020	0.05	0.050	0.050	0.020	0.50
G [#]	ICP/MS	0.010	0.200	0.005	0.05	0.500	0.010	0.060	0.50
H [□]	ICP/MS	0.010	0.100	0.050	0.10	0.100	0.100	0.050	0.50
I [□]	ICP/MS	0.010	0.100	0.050	0.10	0.100	0.100	0.050	0.50
J	ICP/MS	0.100	0.500	0.500	0.50	0.500	0.500	0.100	1.00
K	GF/AAS	0.160	0.110	0.440	1.06	0.090	0.610	0.480	6.70
L [#]	ICP/MS	0.010	0.200	0.005	0.05	0.500	0.010	0.060	0.50
M*	ICP/MS	0.010	0.050	0.020	0.05	0.050	0.050	0.020	0.50

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Table 2

Lab code	Tool	Diffusion coefficients (10^{-6} cm ² /s)															
		Cd		Cr		Co		Cu		Mn		Ni		Pb		Zn	
		Ternay	Thau	Ternay	Thau	Ternay	Thau	Ternay	Thau	Ternay	Thau	Ternay	Thau	Ternay	Thau	Ternay	Thau
A	DGT-OP	4.88	4.99	4.04	4.13	-	-	4.98	5.09	4.67	4.77	4.61	4.71	6.43	6.58	4.87	4.98
B	DGT-OP	4.77	4.82	3.95	3.99	4.65	4.7	4.88	4.92	4.58	4.62	4.52	4.56	6.29	6.35	4.76	4.8
C	DGT-OP	6.09	6.09	5.05	5.05	5.94	5.94	6.23	6.23	5.85	5.85	5.77	5.77	8.03	8.03	6.08	6.08
D	DGT-OP	6.10	6.10	5.10	5.10	6.14	6.14	6.20	6.20	6.02	6.02	6.37	6.37	10.0	10.0	6.10	6.10
E	DGT-OP	4.86	-	4.03	-	-	-	4.97	-	-	-	4.60	-	6.40	-	-	-
F*	DGT-OP	4.88	5.12	4.05	4.25	4.76	5.00	4.99	5.24	4.68	4.92	4.62	4.85	6.43	6.75	4.87	5.11
G [#]	DGT-OP	6.09	-	5.05	-	5.94	-	6.23	-	5.85	-	5.77	-	8.03	-	6.08	-
I [□]	DGT-OP	4.86	-	4.03	-	4.74	-	4.97	-	4.66	-	4.60	-	6.40	-	4.85	-
J	DGT-OP	4.86	-	4.03	-	4.74	-	4.97	-	4.66	-	4.60	-	6.40	-	4.85	-
K	DGT-OP	4.88	5.12	4.045	4.25	4.76	5.00	4.99	5.24	4.68	4.92	4.62	4.85	6.43	6.75	4.87	5.11
L [#]	DGT-RP	4.08		3.38		3.98		4.17		3.92		3.87		5.38		4.07	
M*	DGT-RP	3.41	3.60	2.83	2.98	3.32	3.49	3.49	3.67	3.27	3.44	3.23	3.39	4.49	4.72	3.40	3.58

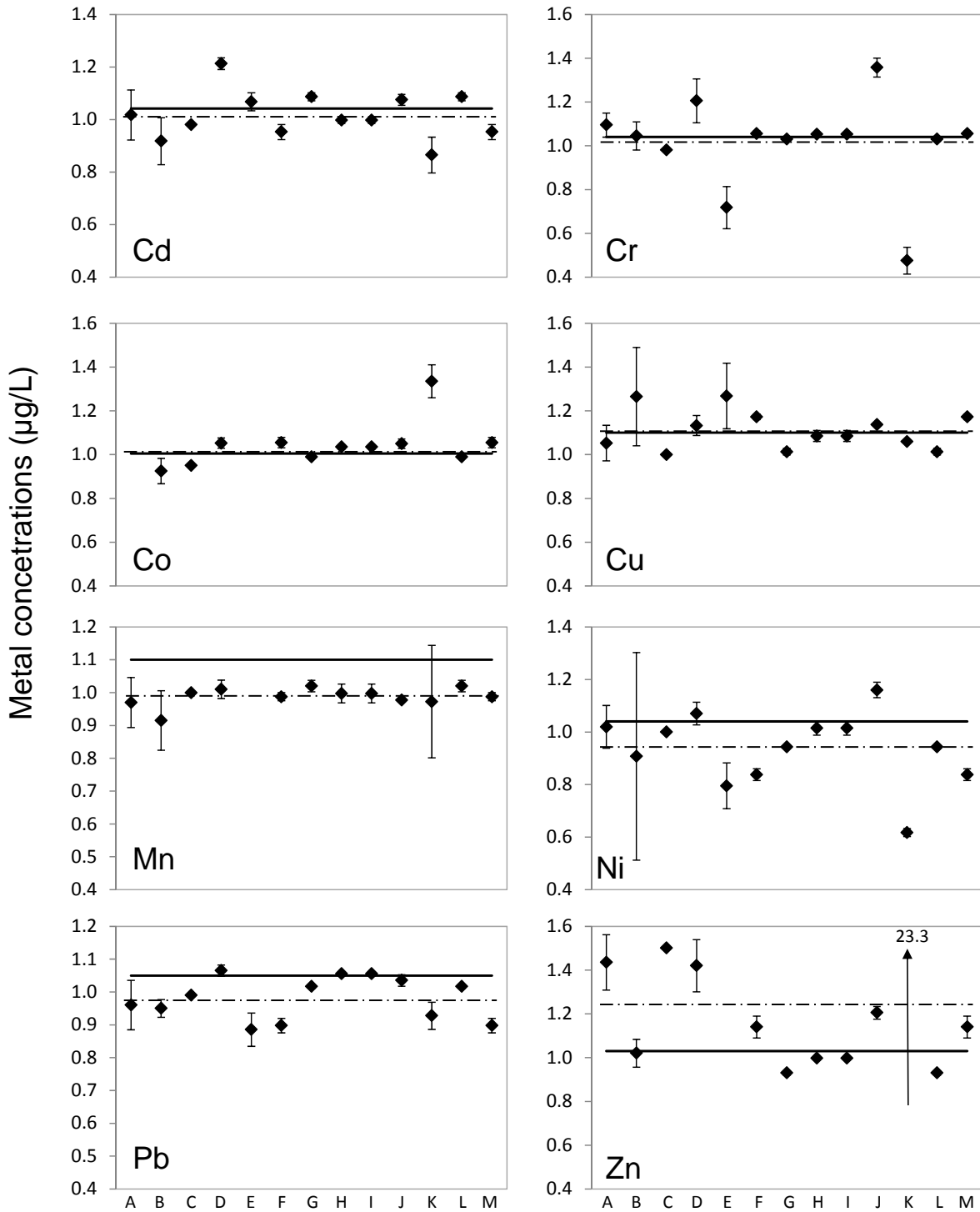
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Table 3

In situ passive sampler data (2010)							SWIFT-WFD proficiency Testing Exercise (2006)			
Metals	Ternay			Thau			LQ Water (µg/L)	Robust mean		
	x* ± SD	RSD	n	x* ± SD	RSD	n		x* ± SD	RSD	n
	(µg/L)	(%)		(µg/L)	(%)			(µg/L)	(%)	
Cd	0.005 ± 0.003	58	12	0.027 ± 0.025	92	7	0.010	0.09 ± 0.08	89	27
Cr	0.076 ± 0.070	93	11	0.036 ± 0.029	80	7	0.050	1.73 ± 1.57	91	36
Co	0.029 ± 0.011	38	9	0.060 ± 0.015	25		0.010	-	-	-
Cu	0.367 ± 0.153	42	13	0.233 ± 0.109	47	7	0.050	4.15 ± 1.66	40	42
Mn	3.47 ± 0.99	28	11	7.48 ± 2.65	35	7	0.100	154 ± 17	11	47
Ni	0.392 ± 0.139	35	13	0.261 ± 0.126	48	7	0.050	1.85 ± 1.40	75	32
Pb	0.063 ± 0.070	112	12	0.021 ± 0.012	58	6	0.010	1.20 ± 0.83	69	31
Zn	1.40 ± 1.10	79	10	3.15 ± 3.13	99	5	0.500	12.3 ± 2.8	23	39

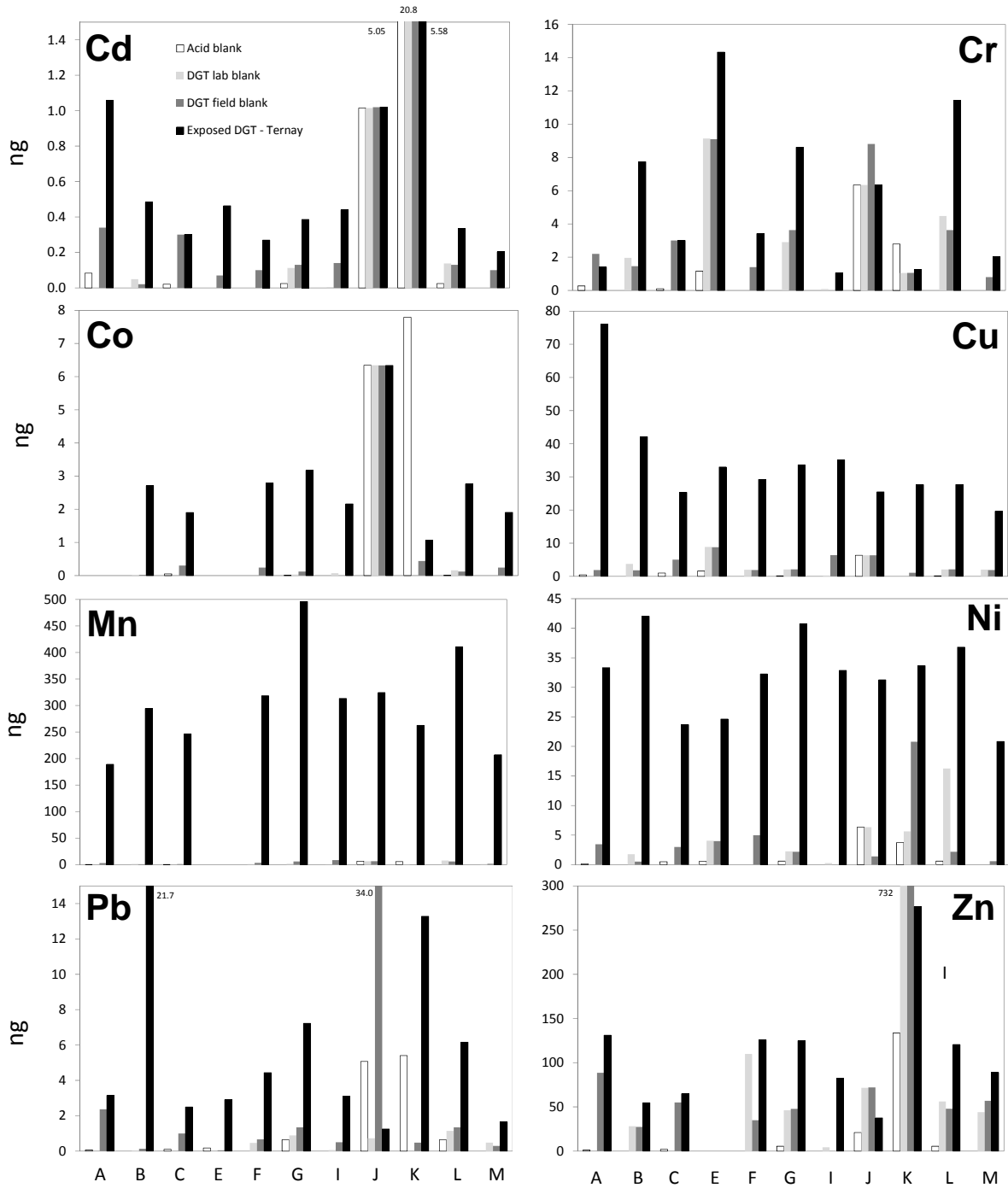
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Table 4



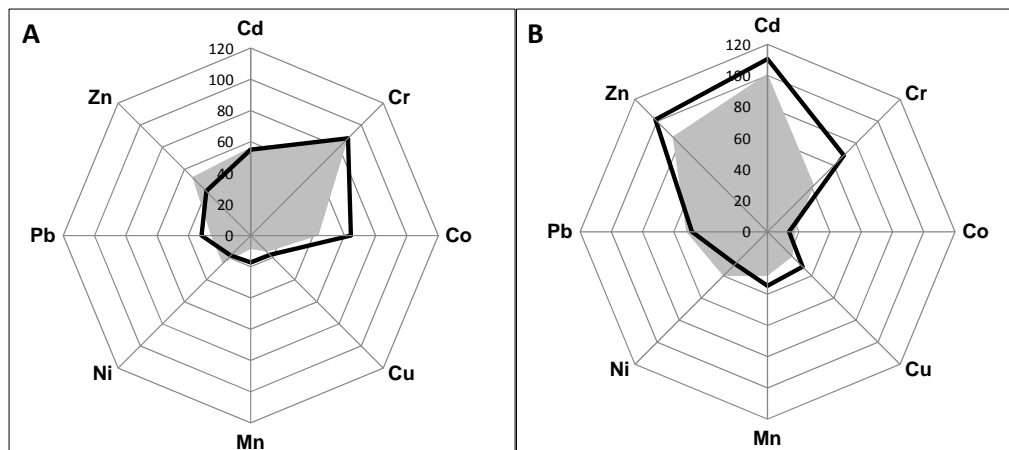
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Fig 1.

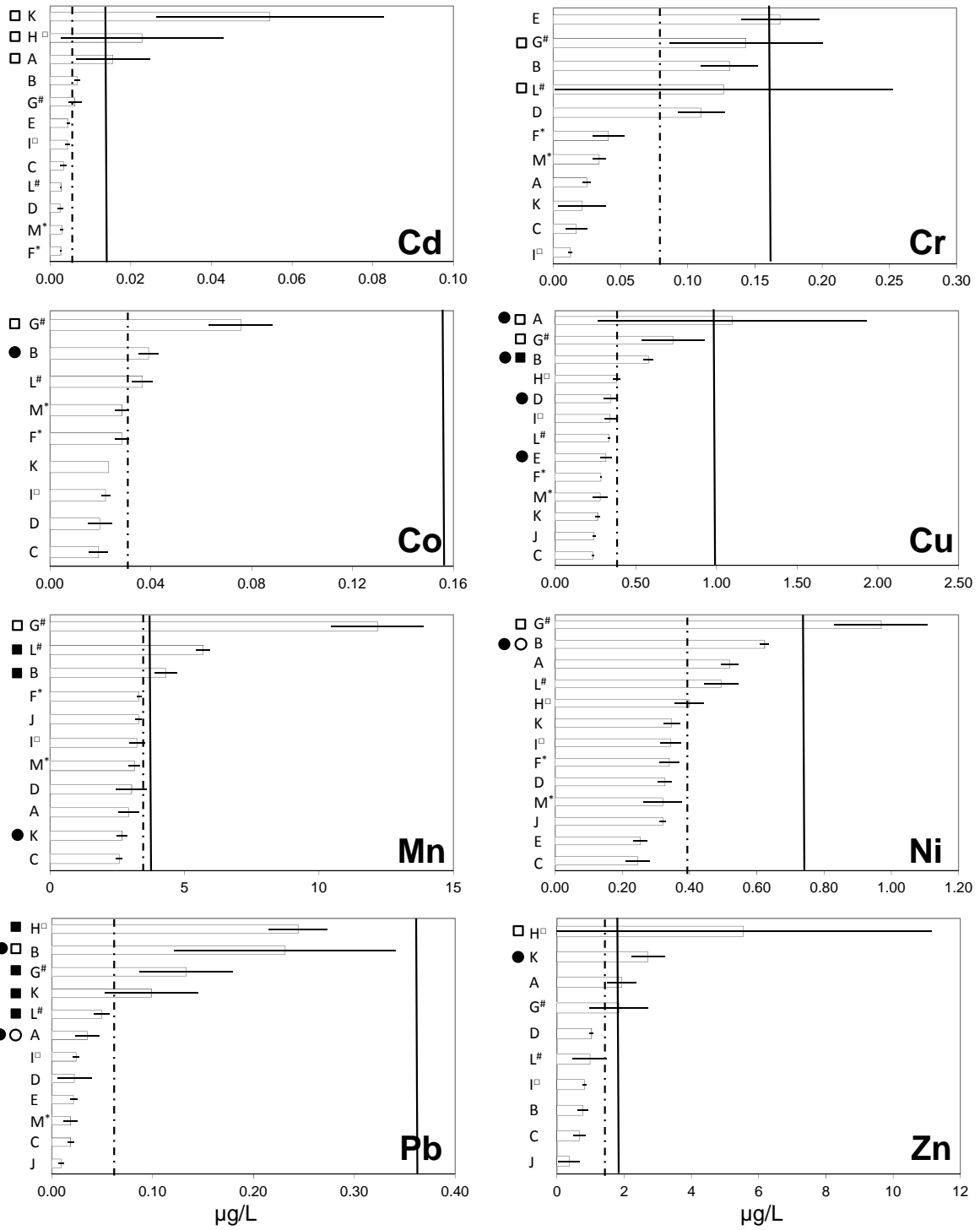


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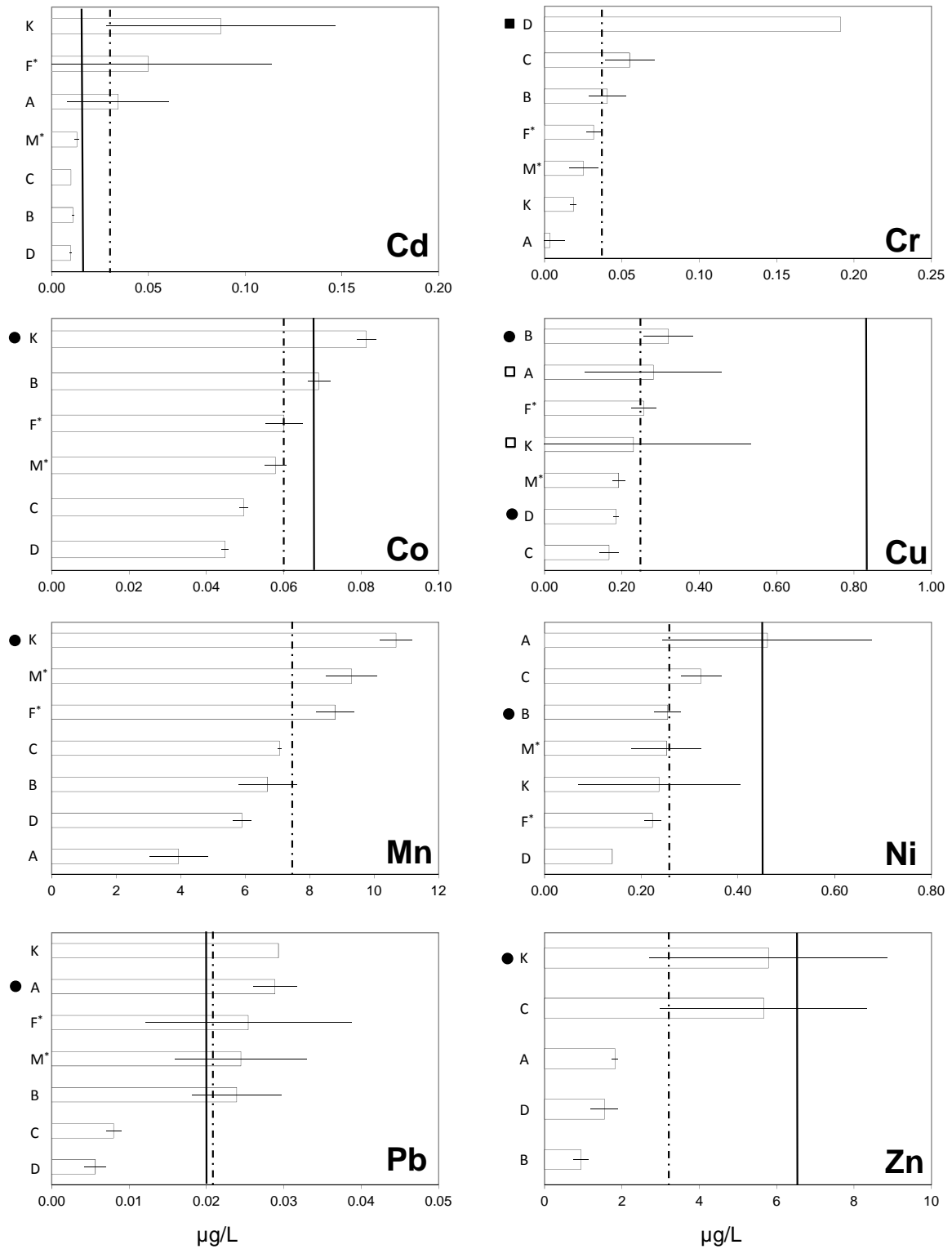
Fig. 2



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Fig. 5